

What is claimed is:

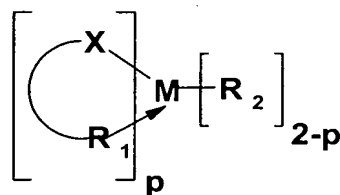
1. A method of producing cyclic olefin polymers having polar functional groups, the method comprising:

preparing a catalyst mixture including

i) a procatalyst represented by formula (1) containing a group 10 metal and a ligand containing hetero atoms bonded to the metal;

ii) a cocatalyst represented by formula (2) including a salt compound which is capable of providing a phosphonium cation and an anion weakly coordinating to the metal of the procatalyst; and

addition-polymerizing cyclic olefin monomers having polar functional groups in the presence of an organic solvent and the catalyst mixture, at a temperature of 80-150 °C:



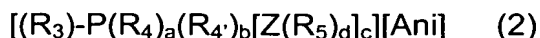
where X is a hetero atom selected from S, O and N;

$R_1$  is  $-\text{CH}=\text{CHR}^{20}$ ,  $-\text{OR}^{20}$ ,  $-\text{SR}^{20}$ ,  $-\text{N}(\text{R}^{20})_2$ ,  $-\text{N}=\text{NR}^{20}$ ,  $-\text{P}(\text{R}^{20})_2$ ,  $-\text{C}(\text{O})\text{R}^{20}$ ,  $-\text{C}(\text{R}^{20})=\text{NR}^{20}$ ,  $-\text{C}(\text{O})\text{OR}^{20}$ ,  $-\text{OC}(\text{O})\text{OR}^{20}$ ,  $-\text{OC}(\text{O})\text{R}^{20}$ ,  $-\text{C}(\text{R}^{20})=\text{CHC}(\text{O})\text{R}^{20}$ ,  $-\text{R}^{21}\text{C}(\text{O})\text{R}^{20}$ ,  $-\text{R}^{21}\text{C}(\text{O})\text{OR}^{20}$  or  $-\text{R}^{21}\text{OC}(\text{O})\text{R}^{20}$ , in which  $\text{R}^{20}$  is a hydrogen, a halogen, a linear or branched  $\text{C}_{1-5}$  alkyl, a linear or branched  $\text{C}_{1-5}$  haloalkyl, a linear or branched  $\text{C}_{5-10}$  cycloalkyl, a linear or branched  $\text{C}_{2-5}$  alkenyl, a linear or branched  $\text{C}_{2-5}$  haloalkenyl, or an optionally substituted  $\text{C}_{7-24}$  aralkyl, and  $\text{R}^{21}$  is a  $\text{C}_{1-20}$  hydrocarbylene;

$\text{R}_2$  is a linear or branched  $\text{C}_{1-20}$  alkyl, alkenyl or vinyl; a  $\text{C}_{5-12}$  cycloalkyl optionally substituted by a hydrocarbon; a  $\text{C}_{6-40}$  aryl optionally substituted by a hydrocarbon; a  $\text{C}_{7-15}$  aralkyl optionally substituted by a hydrocarbon; or  $\text{C}_{3-20}$  alkynyl;

M is a Group 10 metal; and

p is an integer from 0 to 2, and



where each of a, b and c is an integer from 0 to 3, and  $a+b+c = 3$ ;

Z is O, S, Si or N;

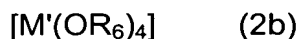
d is 1 when Z is O or S, d is 2 when Z is N, and d is 3 when Z is Si;

R<sub>3</sub> is a hydrogen, an alkyl, or an aryl;

each of R<sub>4</sub>, R<sub>4</sub>' and R<sub>5</sub> is a hydrogen; a linear or branched C<sub>1-20</sub> alkyl, alkoxy, allyl, alkenyl or vinyl; a C<sub>3-12</sub> cycloalkyl optionally substituted by a hydrocarbon; a C<sub>6-40</sub> aryl optionally substituted by a hydrocarbon; a C<sub>7-15</sub> aralkyl optionally substituted by a hydrocarbon; a C<sub>3-20</sub> alkynyl; a tri(linear or branched C<sub>1-10</sub> alkyl)silyl; a tri(linear or branched C<sub>1-10</sub> alkoxy)silyl; a tri(optionally substituted C<sub>3-12</sub> cycloalkyl)silyl; a tri(optionally substituted C<sub>6-40</sub> aryl)silyl; a tri(optionally substituted C<sub>6-40</sub> aryloxy)silyl; a tri(linear or branched C<sub>1-10</sub> alkyl)siloxy; a tri(optionally substituted C<sub>3-12</sub> cycloalkyl)siloxy; or a tri(optionally substituted C<sub>6-40</sub> aryl)siloxy, in which each substituent is a halogen or C<sub>1-20</sub> haloalkyl; and

[Ani] is an anion capable of weakly coordinating to the metal M of the procatalyst represented by formula (1) and is selected from the group consisting of borate, aluminate, [SbF<sub>6</sub>]-, [PF<sub>6</sub>]-, [AsF<sub>6</sub>]-, perfluoroacetate([CF<sub>3</sub>CO<sub>2</sub>]-), perfluoropropionate([C<sub>2</sub>F<sub>5</sub>CO<sub>2</sub>]-), perfluorobutyrate([CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>]-), perchlorate([ClO<sub>4</sub>]-), p-toluenesulfonate([p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]-), [SO<sub>3</sub>CF<sub>3</sub>]-, boratabenzene, and carborane optionally substituted with a halogen.

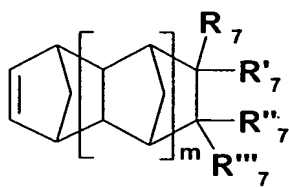
2. The method of claim 1, wherein the borate or aluminate of formula (2) is an anion represented by formula (2a) or (2b):



where M' is B or Al;

R<sub>6</sub> is each independently a halogen, a linear or branched C<sub>1-20</sub> alkyl or alkenyl optionally substituted by a halogen, a C<sub>3-12</sub> cycloalkyl optionally substituted by a halogen, a C<sub>6-40</sub> aryl optionally substituted by a hydrocarbon, a C<sub>6-40</sub> aryl optionally substituted by a linear or branched C<sub>3-20</sub> trialkylsiloxy or a linear or branched C<sub>18-48</sub> triarylsiloxy, or a C<sub>7-15</sub> aralkyl optionally substituted by a halogen.

3. The method of claim 1, wherein the cyclic olefin monomer is a compound represented by formula (3):



(3)

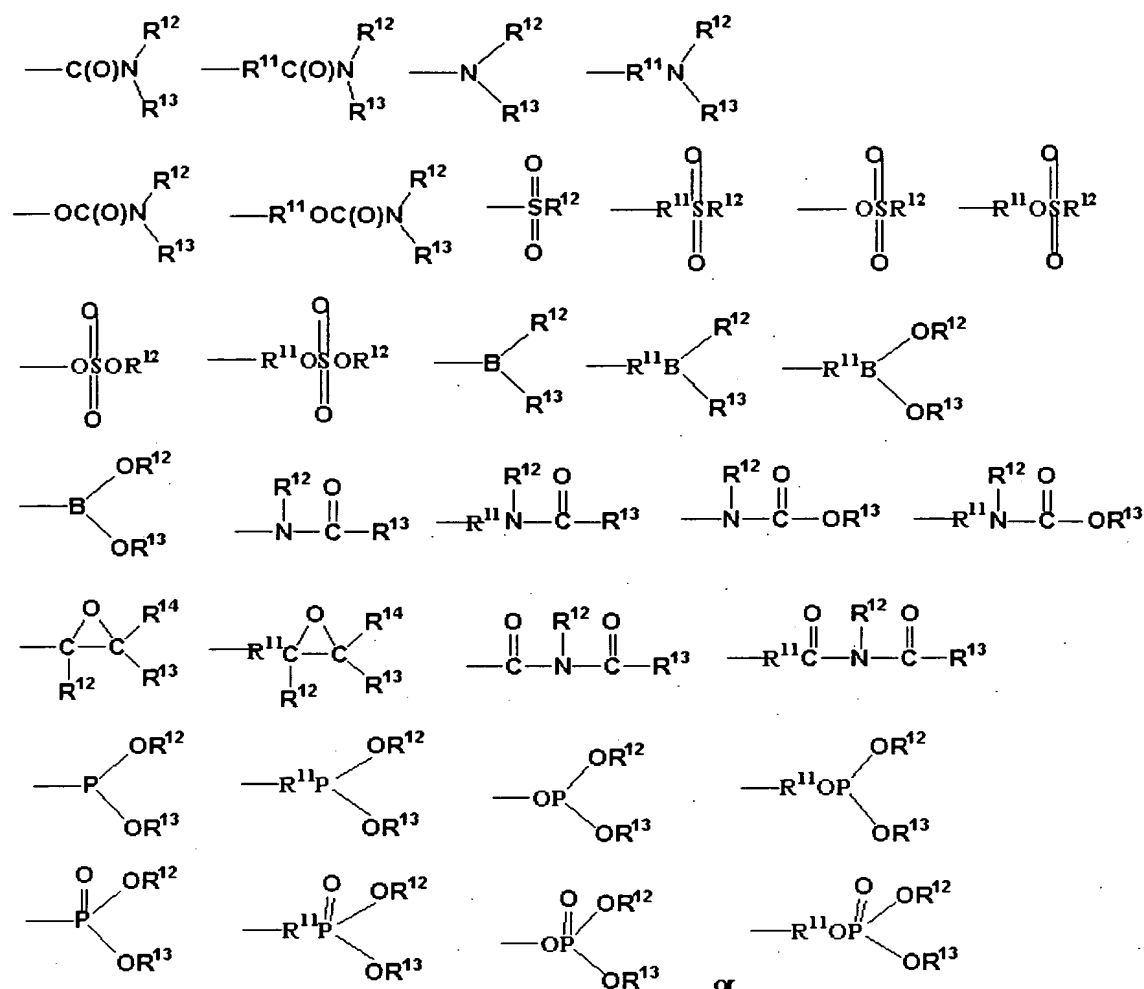
where m is an integer from 0 to 4;

at least one of  $R_7$ ,  $R'_7$ ,  $R''_7$  and  $R'''_7$  is a polar functional group and the others are nonpolar functional groups;

5  $R_7$ ,  $R'_7$ ,  $R''_7$  and  $R'''_7$  can be bonded together to form a saturated or unsaturated  $C_{4-12}$  cyclic group or a  $C_{6-24}$  aromatic ring;

the nonpolar functional group is a hydrogen; a halogen; a linear or branched  $C_{1-20}$  alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched  $C_{3-20}$  alkynyl or haloalkynyl; a  $C_{3-12}$  cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a  $C_{6-40}$  aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a  $C_{7-15}$  aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;

15 the polar functional group is a non-hydrocarbonaceous polar group having at least one O, N, P, S, Si or B and is  $-R^8OR^9$ ,  $-OR^9$ ,  $-OC(O)OR^9$ ,  $-R^8OC(O)OR^9$ ,  $-C(O)R^9$ ,  $-R^8C(O)OR^9$ ,  $-C(O)OR^9$ ,  $-R^8C(O)R^9$ ,  $-OC(O)R^9$ ,  $-R^8OC(O)R^9$ ,  $-(R^8O)_k-OR^9$ ,  $-(OR^8)_k-OR^9$ ,  $-C(O)-O-C(O)R^9$ ,  $-R^8C(O)-O-C(O)R^9$ ,  $-SR^9$ ,  $-R^8SR^9$ ,  $-SSR^8$ ,  $-R^8SSR^9$ ,  $-S(=O)R^9$ ,  $-R^8S(=O)R^9$ ,  $-R^8C(=S)R^9$ ,  $-R^8C(=S)SR^9$ ,  $-R^8SO_3R^9$ ,  $-SO_3R^9$ ,  $-R^8N=C=S$ ,  $-NCO$ ,  $R^8-NCO$ ,  $-CN$ ,  $-R^8CN$ ,  $-NNC(=S)R^9$ ,  $-R^8NNC(=S)R^9$ ,  $-NO_2$ ,  $-R^8NO_2$ ,



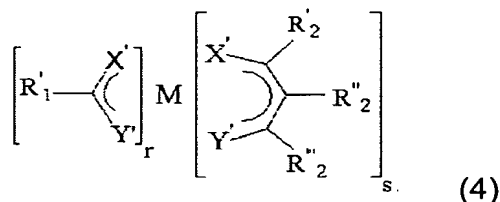
in which each of  $\text{R}^8$  and  $\text{R}^{11}$  is a linear or branched  $\text{C}_{1-20}$  alkylene, haloalkylene, alkenylene or haloalkenylene; a linear or branched  $\text{C}_{3-20}$  alkynylene or haloalkynylene; a  $\text{C}_{3-12}$  cycloalkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a  $\text{C}_{6-40}$  arylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or a  $\text{C}_{7-15}$  aralkylene optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl;

each of  $\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{12}$  and  $\text{R}^{13}$  is a hydrogen; a halogen; a linear or branched  $\text{C}_{1-20}$  alkyl, haloalkyl, alkenyl or haloalkenyl; a linear or branched  $\text{C}_{3-20}$  alkynyl or haloalkynyl; a  $\text{C}_{3-12}$  cycloalkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a  $\text{C}_{6-40}$  aryl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; a  $\text{C}_{7-15}$  aralkyl optionally substituted by an alkyl, an alkenyl, an alkynyl, a halogen, a haloalkyl, a haloalkenyl or haloalkynyl; or an alkoxy, an haloalkoxy, a

carbonyloxy or a halocarbonyloxy; and

k is an integer from 1 to 10.

4. The method of claim 1, wherein the procatalyst represented by formula (1) and the cocatalyst represented by formula (2) are a palladium compound represented by formula (4) and a phosphonium compound represented by formula (5), respectively;



where each of X' and Y' is a hetero atom selected from S and O;

each of R<sub>1</sub>', R<sub>2</sub>', R<sub>2</sub>'' and R<sub>2</sub>''' is a linear or branched C<sub>1-20</sub> alkyl, alkenyl or vinyl; a C<sub>5-12</sub> cycloalkyl optionally substituted by a hydrocarbon; a C<sub>6-40</sub> aryl optionally substituted by a hydrocarbon; a C<sub>7-15</sub> aralkyl optionally substituted by a hydrocarbon; or a C<sub>3-20</sub> alkynyl;

M is a Group 10 metal; and

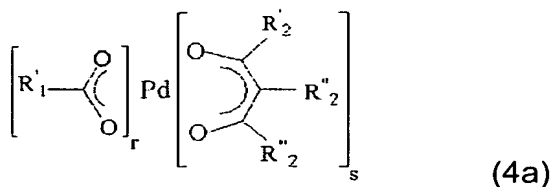
each of r and s is an integer from 0 to 2 and r+s = 2, and



where R<sub>4</sub> is a hydrogen; a linear or branched C<sub>1-20</sub> alkyl, alkoxy, allyl, alkenyl or vinyl; an optionally substituted C<sub>3-12</sub> cycloalkyl; an optionally substituted C<sub>6-40</sub> aryl; an optionally substituted C<sub>7-15</sub> aralkyl; or a C<sub>3-20</sub> alkynyl, in which each substituent is a halogen or a C<sub>1-20</sub> haloalkyl; and

[Ani] is an anion capable of weakly coordinating to the metal M of the procatalyst represented by formula (1) and is selected from the group consisting of borate, aluminate, [SbF<sub>6</sub>]-, [PF<sub>6</sub>]-, [AsF<sub>6</sub>]-, perfluoroacetate([CF<sub>3</sub>CO<sub>2</sub>]-), perfluoropropionate([C<sub>2</sub>F<sub>5</sub>CO<sub>2</sub>]-), perfluorobutyrate([CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>]-), perchlorate([ClO<sub>4</sub>]-), p-toluenesulfonate([p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>]-), [SO<sub>3</sub>CF<sub>3</sub>]-, boratabenzene, and carborane optionally substituted by a halogen.

5. The method of claim 1, wherein the procatalyst represented by formula (1) and the cocatalyst represented by formula (2) are a palladium compound represented by formula (4a) and a phosphonium compound represented by formula (5), respectively;



where each of R<sub>1</sub>', R<sub>2</sub>', R<sub>2</sub>' and R<sub>2</sub>' is a linear or branched C<sub>1-20</sub> alkyl, alkenyl or vinyl; a C<sub>5-12</sub> cycloalkyl optionally substituted by a hydrocarbon; a C<sub>6-40</sub> aryl optionally substituted by a hydrocarbon; a C<sub>7-15</sub> aralkyl optionally substituted by a hydrocarbon; or a C<sub>3-20</sub> alkynyl; and

each of r and s is an integer from 0 to 2 and r+s = 2, and



where R<sub>4</sub> and [Ani] are as defined in claim 4.

6. The method of claims 1, wherein in the procatalyst represented by formula (1), the metal is Pd, p is 2, and the ligand having a hetero atom directly coordinating to the metal is acetylacetonate or acetate, and in the cocatalyst including a salt compound having phosphonium represented by formula (2), b is 0, c is 0, R<sub>3</sub> is H, and R<sub>4</sub> is cyclohexyl, isopropyl, t-butyl, n-butyl or ethyl.

7. The method of claim 1, wherein a molar ratio of the cocatalyst to the procatalyst is 0.5-10:1.

8. The method of claim 1, wherein the catalyst mixture is supported on an inorganic support.

9. The method of claim 8, wherein the inorganic support is at least one selected from the group consisting of silica, titania, silica/chromia, silica/chromia/titania, silica/alumina, aluminum phosphate gel, silanized silica, silica hydrogel, montmorillonite clay and zeolite.

10. The method of claim 1, wherein an organic solvent used to dissolve the catalyst mixture is at least one solvent selected from the group consisting of dichloromethane, dichloroethane, toluene, chlorobenzene and a mixture thereof.

11. The method of claim 1, wherein a total amount of the organic solvent is 50-800% based on the weight of the total monomer in the monomer solution.

12. The method of claim 1, wherein the catalyst mixture comprises a metal catalyst complex composed of the procatalyst and the cocatalyst.

13. The method of claim 1, wherein the catalyst mixture is added in a solid phase to the monomer solution.

14. The method of claim 1, wherein the amount of the catalyst mixture is such that a molar ratio of the procatalyst to the total monomer is 1:2,500 to 1:200,000.

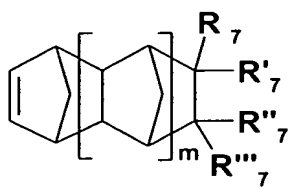
15. The method of claim 1, wherein the monomer solution further comprises a cyclic olefin compound having no polar functional group.

16. The method of claim 1, wherein the cyclic olefin polymers having polar functional groups comprise a cyclic olefin homopolymer, a copolymer of cyclic olefin monomers having different polar functional groups, or a copolymer of a cyclic olefin monomer having a polar functional group and a cyclic olefin monomer having no polar functional group.

17. The method of claim 1, wherein a weight average molecular weight  $M_w$  of the cyclic olefin polymer having a polar functional group is 10,000-1,000,000.

18. The method of claim 1, wherein the monomer solution further comprises a linear or branched  $C_{1-20}$  olefin.

19. A polymer produced using the method of any one of claims 1-18, which is an addition polymer of a cyclic olefin monomer having a polar functional group represented by formula (3) and has a weight average molecular weight  $M_w$  of 10,000-1,000,000:



(3)

where  $m$ ,  $R_7$ ,  $R'_7$ ,  $R''_7$  and  $R'''_7$  are as defined in claim 3.

20. An optical anisotropic film comprising the cyclic olefin polymer having a polar functional group of claim 19.

21. The optical anisotropic film of claim 20, which has a retardation value  $R_{th}$  represented by Equation (1) of 70-1000 nm:

$$R_{th} = \Delta(n_y - n_z) \times d \quad (1)$$

where  $n_y$  is a refractive index of an in-plane fast axis measured at 550 nm;  
 $n_z$  is a refractive index in a direction through the film thickness measured at 550 nm, and  
 $d$  is a film thickness.

22. The optical anisotropic film of claim 21, which is a negative C-plate type optical compensation film for liquid crystal display, satisfying a refractive index requirement of  $n_x \cong n_y < n_z$ , in which  $n_x$  is a refractive index of an in-plane slow axis,  $n_y$  is a refractive index of an in-plane fast axis, and  $n_z$  is a refractive index in a direction through the film thickness.